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Cu Precipitations at the Surface of Crystalline Cu – Zr Alloys after Annealing in Hydrogen*

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Crystalline Cu-Zr alloys of various composition were annealed (200 - 400°C) in ultrahigh vacuum and in hydrogen, and their surface composition was analyzed by X-ray photoelectron spectroscopy. Contrary to the mostly observed oxygen induced surface segregation of Zr we found strong Cu segregation after annealing Cu-rich samples in hydrogen atmosphere. Scanning electron micrographs show surface Cu precipitates, apparently formed under the effect of the heat of chemisorption of hydrogen on Cu.

Introduction

Amorphous and also crystalline alloys of Cu with the d-transition metals Zr, Ni and Pd have been studied quite intensively for the last few years among other reasons because of their special dynamical and diffusional properties in the bulk and at the surface which results in interesting catalytic and hydrogen sorption phenomena [1-15].

Studies of the electronic structure of amorphous $\text{Cu}_x\text{Zr}_{1-x}$ alloys reveal that in the middle of the glass forming range (20 - 75 at% Cu), i.e. around 50 at% Cu, the Fermi level E_F is situated in the Zr 4d band and there is no tendency for ordering. At Cu concentrations > 80 at %Cu E_F shifts to the edge of the Zr 4d band so that the density of states $N(E_F)$ gets drastically reduced to s-band values, in agreement with a sign reversal of the Hall coefficient [1] and increased tendency for local order. These drastic changes of electronic properties are interrelated to total energy changes and structural instabilities and relaxation effects [2]. Activation energies for metal atom diffusion in amorphous Cu - Zr alloys are rather small, by far smaller than for recrystallization, implying that recrystallization is limited by nucleation rather than surface diffusion [3]. The enthalpy variation upon crystallization amounts to 5 kJ/mol [4].

As many other intermetallic compounds also alloys of Cu with d-transition metals show surface segregation effects. The rather high mobility of the metal atoms guarantees to reach thermodynamic equilibrium composition at the

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surface more easily than in other alloys. Indeed, the solid solution system $\text{Cu}_x\text{Ni}_{1-x}$ is the best studied surface segregation alloy [6-8]. On the clean surface segregation of Cu is observed for compositions $0 < x < 0.75$ and Ni segregation is observed at the Cu-rich end of the compositional range. Electronic theory based on a tight binding Hartree approximation is capable of explaining this crossover by preserving charge neutrality [6] in a comparable model by Mukeherjee et al. [7], in which crossover is absent. Cu enrichment was also observed in the topmost surface layers of single crystalline Cu_3Ni_7 and $\text{Cu}_{24}\text{Ni}_{76}$ after annealing at 700 to 800 K and after sputtering [8].

Oxygen chemisorption leads to the "normal" surface segregation by selective oxydation of the more reactive component (Zr). Activated bimetallic Zr-Ni catalysts thus consist of active Ni metal clusters dispersed on Zr oxide support, both of which are supported on the underlying bulk intermetallic alloy [9]. At temperatures around 400° surface enrichment of Ni in the form of NiO and Ni is found after annealing of ZrNi_3 in O_2 and H_2 , resp. [9]. Preferential oxydation of Zr and Zr enrichment at the surface was also observed upon oxygen exposure of amorphous Cu-Zr alloys of various compositions [10].

Whereas surface segregation effects induced by oxygen are known to be strong and important e.g. for bimetallic catalyst, activation of hydrogen storage materials and getters [9,11-13], surface effects induced by the adsorption or absorption of hydrogen are usually rather weak or absent [12,13,14]. In the case of Cu-d transition metal alloys, however, the results on hydrogen induced surface phenomena are rather controversial [14]. Hydrogen adsorption reduces the Cu segregation of Cu-Ni alloys as compared to clean surfaces, in agreement with theory [15]. Strong surface enrichment of Cu and Pd was found upon hydrogen exposure of amorphous Cu-Zr and Pd-Zr, resp., around 200C, but on the Pd and Cu rich side only [14,16]. It was argued recently that this unusual Cu segregation is characteristic of amorphous alloys and does not exist on crystalline alloys. In view of the importance of these segregation effects and their potential application, e.g. in the preparation of bimetallic catalyst, we have studied hydrogen adsorption phenomena on crystalline Cu-Zr alloys.

Photoelectron spectroscopy was used to investigate the surface composition after various treatments of the alloys in an ultrahigh vacuum system. The formation of Cu precipitates was observed after annealing of Cu rich samples in hydrogen. Scanning electron micrographs show that the precipitates reach μm diameter.

Experimental

Cu forms with Zr many intermetallic compounds. The congruently melting compounds are CuZr_2 (MoSi_2 type structure [17]) and Cu_3Zr or $\text{Cu}_{51}\text{Zr}_{14}$ ($\text{Ag}_{51}\text{Gd}_{14}$ type structure [17]) according to older [18] and newer [19] phase diagrams, respectively. We have prepared alloys of the composition Cu_3Zr ,

$\text{Cu}_3\text{ZrO}_{0.04}$, $\text{Cu}_{51}\text{Zr}_{14}$ and CuZr_2 by RF levitation melting in a water cooled Cu crucible at $5 \cdot 10^{-7}$ mbar the constituents Cu (99.99%, Johnson-Matthey), Zr (99.9%, Johnson-Matthey) and in the case of $\text{Cu}_3\text{ZrO}_{0.04}$ some CuO (99.9%, Merck). Guinier X-ray patterns of CuZr_2 and $\text{Cu}_{51}\text{Zr}_{14}$ agree with those reported in the literature [17], the patterns of Cu_3Zr and $\text{Cu}_3\text{ZrO}_{0.04}$ show additional lines probably due to the presence of Zr richer compounds. The lines of ZrO_2 and of Cu are absent.

Heat treatment and surface analysis of the samples were performed on a VG Escalab 5 spectrometer at base pressure $1 \cdot 10^{-10}$ mbar using MgK α radiation of 1254 eV (Au 4f at 84.0 eV, 1.2 eV FWHM). The spectrometer is equipped with a high pressure cell, fracture stage, heating and sample cleaning (diamond file, Ar⁺ bombardement) facilities. Thus all sample treatment was performed inside the ultrahigh vacuum (UHV) spectrometer avoiding the transfer of the sample at air between treatment and analysis.

Micrographs of some samples were taken by a scanning electron microscope.

Results and Discussion

Typical precipitates observed after 10 to 15^h annealing at 200°C and 1 bar H₂ of previously UHV-cleaned samples of Cu_3Zr , $\text{Cu}_3\text{ZrO}_{0.04}$ and $\text{Cu}_{51}\text{Zr}_{14}$ are shown in Fig. 1. The alloy surface is covered to a high degree with precipitates of 0.1 to 1 μm diameter. Analysis of the characteristic X-rays by EDAX and XPS data reveal that the precipitates are of pure Cu. Those samples are Cu coloured, contrary to the grey-metallic colour of the fractured samples.

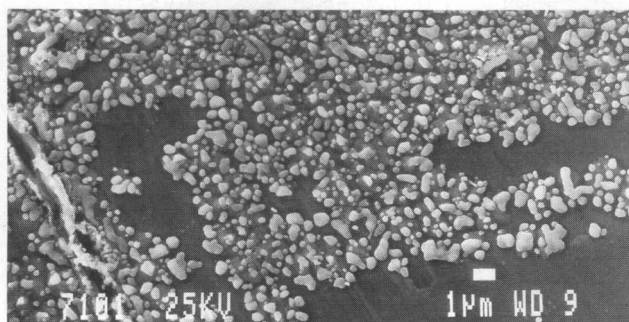


Fig. 1: SEM micrograph of a Cu_3Zr alloy (UHV fractured, 10 hours annealed at 200°C at 1 bar H₂) showing the spherically shaped surface Cu precipitates.

It is questionable whether hydrogen chemisorption is responsible for this Cu segregation and it is interesting to learn what happened to Zr. Surface analysis by XPS should give the answer.

Typical Zr3d photoelectron spectra and Cu : Zr ratios are shown in Fig.2. The more bulk or subsurface (B) and the more top surface (S) sensitive ratios as evaluated from Cu3p and Cu2p core level peaks, respectively, are indicated as well as the colour. Air exposed samples show heavily oxidized Zr and a rather strong Cu enrichment at the surface (Cu : Zr (S) = 6.22 :1). The Zr3d binding energy (BE) of 182.5 eV is smaller than that of ZrO₂ pointing to a suboxide.

UHV clean surfaces are Zr rich. Annealing in UHV (200° for 10^h) causes some oxidation of Zr due to oxygen diffusion from bulk to surface and due to the reaction with residual gas. A mixture of Zr suboxide and Zr metal is found. Furthermore annealing brings along a strong Zr enrichment in the near surface region and relative to the latter one a Cu enrichment on top of the surface.

No Cu precipitates and no Cu colour were found on the air exposed, UHV cleaned and UHV annealed samples, respectively.

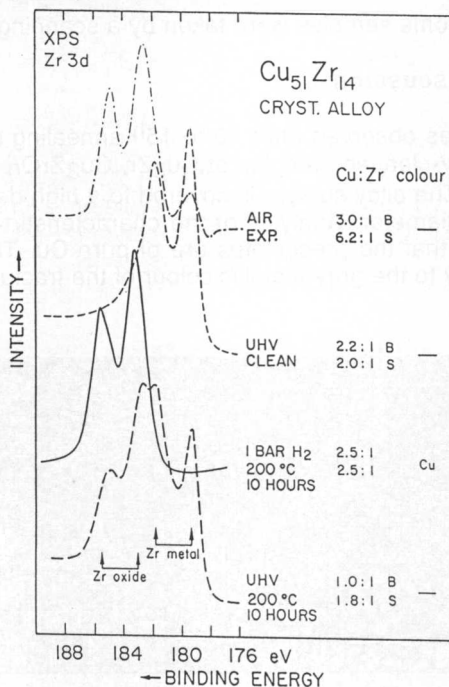


Fig. 2: Photoelectron spectra of the Zr3d core levels of crystalline Cu₅₁Zr₁₄ after various sample treatments. The Cu : Zr atomic ratios S and B were evaluated using the largely top surface sensitive Cu2p peak (S) and the largely bulk sensitive Cu3p peak (B), respectively.

Annealing in hydrogen (1 bar H₂, 200°C, 10^h) causes full oxidation of

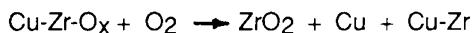
all surface and near surface Zr into ZrO₂ and does not significantly affect the Cu : Zr ratio, although the sample changes completely to Cu colour in a surface layer of several tenth of a millimeter thickness. On some samples a splitting of the Cu core level peaks was observed apparently due to the formation of some electrically isolated Cu precipitates which get charged upon photoelectron emission.

Apparently annealing in UHV leads to the normal, fast, oxygen induced surface segregation of Zr with the formation of ZrO₂ at the surface, whereas annealing in hydrogen ends up in a surface disproportionation of Cu-Zr alloys into ZrO₂ and Cu precipitates. In order to analyse the influence of time and temperature, hydrogen and oxygen partial pressure as well as of the alloy composition on the formation and size of the Cu precipitates annealing of various samples at temperatures up to 400°C at 0.1 to 30 bar H₂ during 0.5 to 50^h was studied. Detailed results will be published elsewhere; they can be summarized as follows:

- no surface Cu precipitates are formed on the Zr rich compound CuZr₂.
- minor differences were only observed between Cu₅₁Zr₁₄ and Cu₃Zr.
- size and number of particles per unit surface area depend on the annealing parameters time, temperature, and pressure.
- the unannealed air exposed samples show a rather high oxygen content down to 100 nm depth.
- samples with additional oxygen (Cu₃ZrO_{0.04}) show similar Cu precipitates.

Based on the above results we suggest the following mechanism:

The Cu rich alloys have a rather high oxygen content. The oxygen is dissolved in the metal matrix or present in a ternary suboxide. Residual gas and hydrogen gas are further sources of oxygen. Elevated temperature favours the formation of the thermodynamically more stable ZrO₂ by a disproportionation reaction of the type



Upon annealing in UHV Zr is selectively oxidized and strongly enriched on top of the surface, i.e. Cu is covered by ZrO₂. The presence of hydrogen blocks the Zr enrichment and the free surface Cu forms precipitates, possibly favoured by the heat of hydrogen chemisorption on Cu. Similar disproportionation of FeTi with the formation of surface Fe precipitates was observed earlier [20].

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